Chlorophenolic and isotopic tracers of pulp mill effluent in sedimenting particles collected from southern lake saimaa, Finland

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Abstract

Sediment traps were used to collect settling particles at two stations upstream of a pulp and paper mill and at four stations along the effluent gradient in Southern Lake Saimaa. The particle samples were collected monthly from May to October 1991. Trap materials were analyzed for concentration and stable isotopic composition of organic carbon and nitrogen. The May 1991 trap samples and water and surface sediment samples from the trap locations were also analyzed for chlorophenolics. The trapped particle flux in May was 6.4 g(dry wt.)/m^2/day at the station closest to the pulp mill (3.3 km) and decreased to 2.6 g(dry wt.)/m^2/day at the farthest station (16.1 km). The organic carbon content of the particles varied from 10.5% to 22.1% and was the highest at the station nearest to the mill. There was a strong point source signal in the nitrogen isotope composition of effluent material. The other sampling times revealed a similar pattern. The total concentration of chlorophenols, chloroguaiacols and chlorocatechols was 0.8, 17.1 and 16.3 μg/g (dry wt.) particles, respectively, at the nearest station and decreased downstream. The total extractable organic halogens in particles exhibited a similar concentration pattern to the identified chlorinated compounds. While about 60% of chloroguaiacols and about 90% of chlorocatechols are removed by sedimentation or degradation processes in the recipient area, most of the chlorophenols and adsorbable organic halogens are transported through the system.

Keywords: Pulp mill effluent; Suspended particles; Sedimentation; Chlorophenols; Carbon isotopes; Nitrogen isotopes; Stable isotopes; δN^{15}; δC^{13}

1. Introduction

In natural waters, suspended particulate matter affects the fate and cycling of many constituents. Association with settling particles controls the water column residence times and concentrations of highly hydrophobic organic contaminants such as chlorinated biphenyls and polycyclic aromatic hydrocarbons [1–3] as well as many trace metals [4,5]. Materials are cycled in a two stage process: relatively rapid settling of constituents associated with particulate matter and incorporation into the bioturbated layer of surface sediments. The depth

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of the bioturbated or bioactive layer of the sediment varies a lot and depends on the benthic community present on the site. Subsequently these constituents are available for reintroduction into the water column or food web, on seasonal to decadal time scales, through uptake by benthos [6–8] or resuspension [2,5].

Sediment traps have been used in several studies to investigate the sedimentation and resuspension rates in different areas and to characterize the sedimenting and resuspended particles [9–13]. The chemical composition of particles suspended in water column may vary depending on the time of the year and area under study [5,14]. For example, pulses of terrestrial runoff, algal blooms, or strong resuspension events all strongly influence particle composition.

The partitioning of organic xenobiotics between water and suspended particles has been found to be related to the organic content in both phases [15]. The organic carbon content of the particulate matter is the most important factor in determining the sorption properties of the particles. In most cases, the partition coefficient is demonstrated to increase with the increasing hydrophobicity of the xenobiotics and amount of organic matter in sediment [16–18]. However, the role of the structural properties of the natural organic matter associated with the particles has not been evaluated. In the case of dissolved organic matter, changes in the structure can alter the observed partition coefficient even on a carbon normalized basis [19–22].

Pulp mill effluent discharged into a receiving water system contains different types of particles, macromolecules (often called chlorolignin), metals (e.g. Zn, Al, Cu) and organic chemicals [23,24]. In the effluent and in the receiving water interactions can occur between the effluent components themselves, or between natural particles or humic substances and effluent components. Besides the chemical-particle interactions, chlorolignin may bind the small molecular weight compounds in the effluent and transport them further from the mill [25] or chlorolignin may be bound by the particles suspended in water [26]. All these interactions affect the environmental fate of the chemicals in the effluent.

The objectives of this part of the large ECOBALANCE project were (1) to measure the sedimentation along a transect aligned with the direction of flow through the receiving waters, (2) to characterize the material collected from sediment traps, and (3) to estimate the effect of sedimentation on the environmental fate of some chlorinated compounds discharged from the pulp mill.

2. Materials and methods

2.1. Sample collection

The pulp mill under study is situated on the southern shore of Lake Saimaa, Finland, (Fig. 1) and produced Cl_2/ClO_2 (20–30%/70–80%) bleached pine and birch kraft pulp in 1991. Effluent waters (1.5 m^3/s) are treated in an aerated lagoon before entering the recipient. Recipient flow past the mill outflow is approximately constant (forced by a pump station upstream) at 40 m^3/s. The mill discharges into a complex, island filled lagoon, before entering the main basin of Lake Saimaa, a large (4380 km^2), relatively shallow (14 m average depth) convoluted basin.

Sediment traps (3 glass tubes: ϕ 5 cm, height 50 cm, Fig. 2) were used to collect settling materials at four stations along an effluent gradient and at two stations upstream of the pulp mill (Fig. 1). The traps were placed 2 m above the bottom on the areas where over all water depth was 12–15 m. This set up was assumed to be adequate although resuspension under these conditions are hard to estimate [11]. The trap samples were collected monthly from May to October 1991. No poisons were used to preserve the trapped material. The collected samples were transported to the laboratory in cold boxes, were freeze dried and weighed within 3 days after collection. Samples were stored in a freezer prior to further analysis.

Water samples were collected from the treated mill effluent and from recipient waters, during the first trap deployment period only, at one site upstream from the mill (Station 2, Fig. 1) and at the downstream sites where sediment traps were placed. In the autumn of 1990, sediment samples were taken from the trap locations using an Ekman-type sampler and other water samples were also collected at this time.
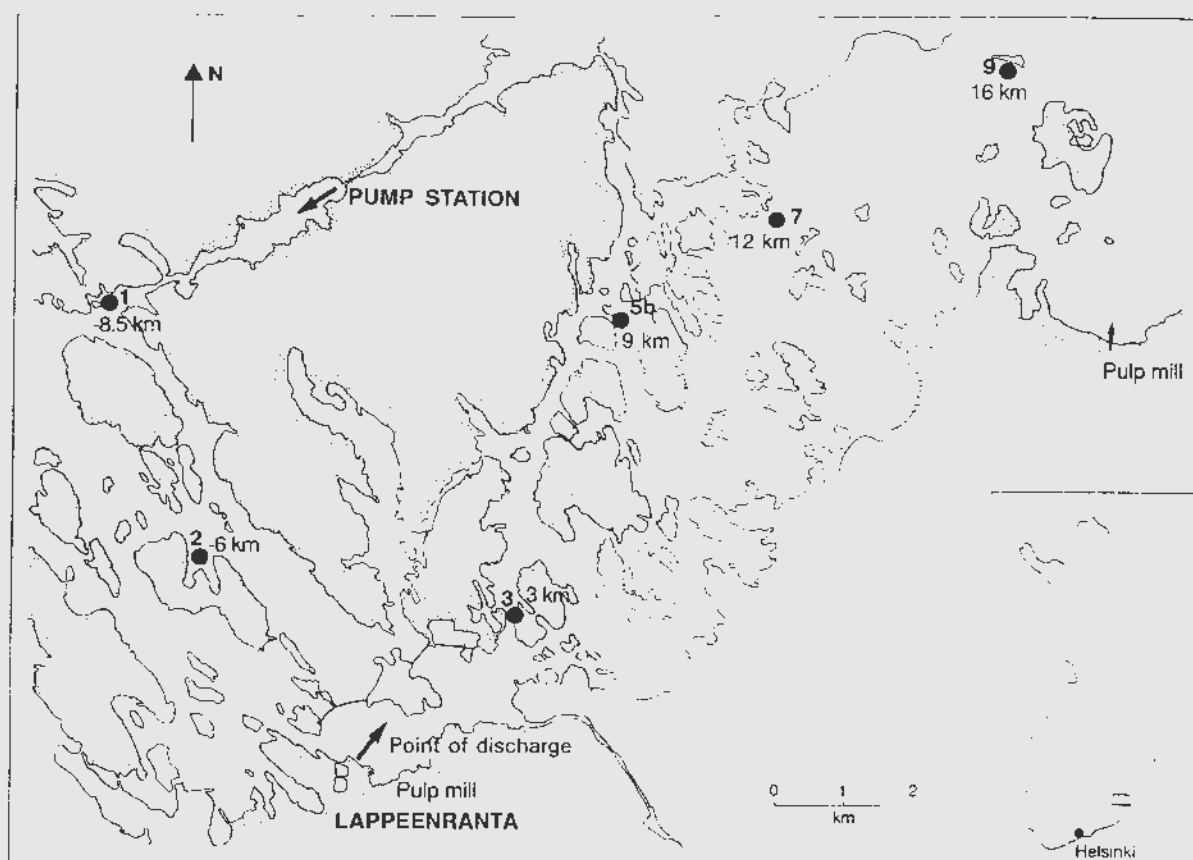
Fig. 1. A map showing the sampling stations near the pulp mill on Lake Saimaa, Southern Finland. Distances (in km) from the outfall are indicated.

2.2. Characterization of particles and analysis

Samples for organic carbon and nitrogen analysis were ground, acidified with 1 N HCl, and mixed on a shaker table overnight to remove $CaCO_3$. They were then oven dried at 90°C and stored in a desiccator prior to analysis. Dried particle, trap and sediment samples were analyzed for organic carbon and nitrogen content (Carbo Erba elemental analyzer model 1106). The loss on ignition (500°C, 4 h) was measured for the particle sample.

Aliquots of these carbonate-free sediment samples were prepared for isotope analysis by high temperature combustion. The sediments were

weighed into 9 mm Vycor tubes which had been precombusted at 900°C. Precombusted CuO wire and Cu powder were added to the tubes which were then evacuated and flame sealed. The samples were combusted at 850°C for 2 h, cooled to 600°C for 2 h, then cooled to ambient temperature overnight. Gases were purified by cryogenic vacuum distillation; H_2O was frozen into a dry-ice 2-propanol trap (−80°C), CO_2 was frozen into a sample tube immersed in liquid nitrogen and nitrogen frozen into a sample bulb, containing silica gel, at liquid nitrogen temperature. Carbon quantified by manometry during this process agreed (to $< \pm 5\%$) with CHN results. Stable isotopes were analyzed using a VG PRISM mass spectrometer.
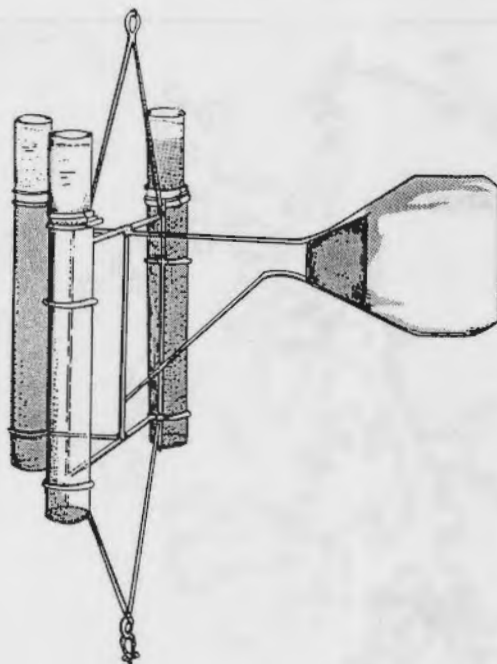
Fig. 2. The sediment trap device consisting of a metal frame and plastic holders for glass tubes.

Stable isotope ratios were calculated as follows:

$$x^{13}C \; (\permil) =$$

$$\left[\frac{R \text{ (sample)} - R \text{ (standard)}}{R \text{ (standard)}} - 1 \right] * 1000$$

where $R = C^{13}/C^{12}$; with an analogous formula for nitrogen. Data are reported relative to the PDB standard for carbon and air for nitrogen. Precision (1 standard deviation) for triplicate analyses of standard materials was $<0.1 \; \permil$ for carbon and $<0.2 \; \permil$ for nitrogen. One quarter of the samples were run in duplicate and all of the data were within, the above stated, one standard deviation.

Total chlorophenolics (i.e. bound + free) were measured for the May 1991 particle samples and the autumn of 1990 sediment samples. To prevent an oxidation of phenols to quinones, a small amount of ascorbic acid was added to a preweighted sample (200–300 mg). After that, the

sample was hydrolysed in sealed tubes, containing 2 ml of 2.5 M KOH in 50% ethanol, at 70°C for 16–18 h after nitrogen purging. The tubes were cooled, centrifuged and the supernatant collected. The residue was rinsed once with an additional 2 ml of ethanolic KOH solution. The supernatants were combined and diluted with distilled water. A part of hydrolysate was acidified with sulphuric acid and extracted with diethyl ether before acetylation of chlorophenolics and GC analysis with EC-detection. The other part of the hydrolysate was diluted up to 50 ml and total organically bound halogens (SOX) were analyzed by SCAN-W 9:89 method [27] with Dohrmann DX-20B analyzer.

Free chlorophenolics in a water sample were acetylated prior the extraction with hexane and GC analysis with EC-detection. Absorbable organically bound halogen (AOX) was analyzed according to the SCAN-W 9:89 method [27].

3. Results

The pulp and paper mill effluent (characteristics in Table 1 and 2) contributed to the concentrations of dissolved organic carbon (DOC), adsorbable organic halogens (AOX), and sodium (Table 3) as well as the concentration of chlorophenolics (Fig. 3; Appendix 1) in recipient water. All of these parameters showed a clear increase between stations 2 (background, 6 km upstream from the mill) and 3 (3.3 km downstream from the mill), then exhibited a decrease with the distance from the discharge. Concentrations of DOC decreased downstream and returned to background levels by station 9, which is 16 km from the mill. The suspended particle concentration, measured in 1990 [25], also decreased to background by station 9. When we use the organic carbon concentration of trapped material as an estimate of the particulate organic carbon on the 1990 samples, then only 1–5% of the organic matter is in the particulate form throughout the study region, while the remainder is dissolved. The concentration of the free chlorophenolics in the water (Fig. 3) remain at least a factor of 2 above background levels at the 16 km station. The only loss mechanism of chlorophenols explored in this study is sedimenta-

Table 1
Characterization of the pulp mill effluent discharged to the recipient under study

	AOX (mg/l)	pH	Cond. (mS/m)	Na+ (mg/l)	Susp. Solids (mg/l)	Ash (%)	COD (mg/l)	BOD7 (mg/l)
May-91								
Mean	16.31	7.7	167	230	83	32.1	743	100
Min.	12.49	7.3	145	196	28	23.0	530	58
Max.	18.81	7.8	183	256	113	71.0	882	129
June-91								
Mean	13.22	7.8	153	217	76	39.1	582	68
Min.	5.95	7.4	104	156	39	29.0	309	29
Max.	16.75	8.0	176	244	121	53.0	803	140

Values are averages, minimum and maximum for May and June 1991 measured once every day of the month by the analytical laboratory of Kaukas Ltd., Kymmene Corporation.

tion, although these compounds do undergo microbial and chemical decay [28–32] or may evaporate into the atmosphere.

3.1. Traps

The maximum sedimentation is greater downstream from the mill compared to upstream Station 2 (Fig. 4) High sedimentation at station 1

Table 2
Chlorophenolics in the treated pulp mill effluent (μg/l)

Compound	Conc. in effluent (μg/l)
246-TCP	7.1 ± 1.3
2346-TeCP	1.1 ± 0.3
PCP	0.3 ± 0.1
45-DCG	4.3 ± 3.3
345-TCG	46.8 ± 6.1
456-TCG	7.4 ± 1.0
3456-TeCG	8.6 ± 1.1
345-TCC	19.0 ± 5.2
3456-TeCC	6.4 ± 2.7

246-TCP = 2,4,6-trichlorophenol; 2346-TeCP = 2,3,4,6-tetrachlorophenol; PCP = pentachlorophenol; 45-DCG = 4,5-dichloroguaiacol; 345-TCG = 3,4,5-trichloroguaiacol; 456-TCG = 4,5,6-trichloroguaiacol; 3456-TeCG = 3,4,5,6-tetrachloroguaiacol; 345-TCC = 3,4,5-trichlorocatechol; 3456-TeCC = 3,4,5,6-tetrachlorocatechol.
The values are means (±S.D.) from 10 samples taken between April 30-May 31, 1991.

is likely due to high turbulence created by water flow through the narrow water way from the pump station (Fig. 1). The rates of collection of settling materials within the sediment traps increased substantially between stations 2 and 3. In order to be trapped, this implies that some of the particulate effluent from the mill is settling fairly rapidly. Generally, the mass fluxes have returned to background (station 2) levels by station 9 (16 km from the mill).

The particles collected in the traps downstream from the mill are rich in organic matter as shown by the approximately 1.5–2 times increase in or-

Table 3
Dissolved organic carbon (DOC), suspended particle, adsorbable organic halogen (AOX) and sodium concentrations along the recipient area on September 1990 and May 1991 sampling

Station (km)	DOC mg/l		Particle mg/l	AOX μg/l		Na+ mg/l	
	1990[a]	1991	1990[a]	1990[a]	1991	1990[a]	1991
−8.5	7.2	na	0.9	60	na	3.6	na
−6	na	6.9	na	na	40	na	2.94
3	14.7	22.9	3.9	600	520	18.3	13.08
9	14.4	11.5	3.5	498	540	17.3	12.98
12	10.4	9.4	2.4	364	190	12.4	8.88
16	8.2	8.1	1.0	248	680	8.6	6.79

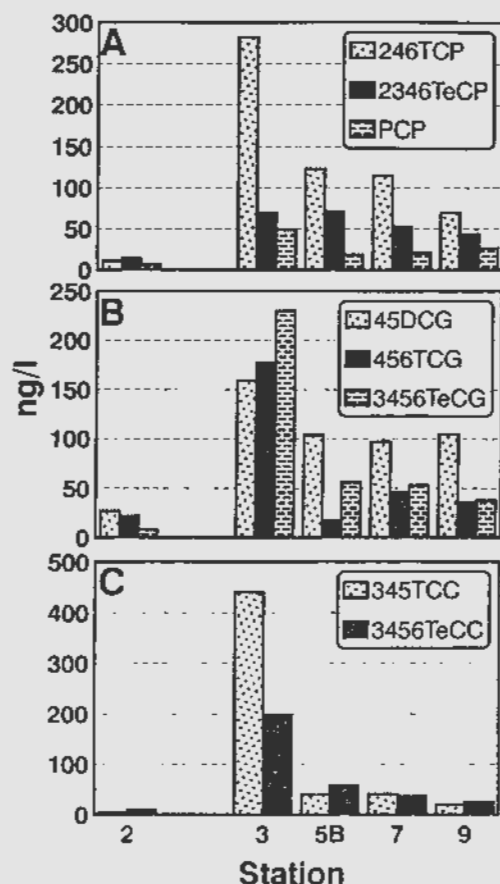[a]Data from Kukkonen 1992 [25].
Na, not analysed.

Fig. 3. The concentrations of different chlorinated phenols (A) guaiacols (B) and catechols (C) in water samples during the 'May' 1991 sampling period. The bars represent a mean of four analyses. For the codes, please see Table 2.

ganic carbon and nitrogen between traps located at stations 2 and 3 (Tables 4 and 5). No seasonality was observed in these parameters under the pulp mill. Both organic carbon and nitrogen content of sedimenting particles were higher than the concentration in the bottom sediments. There is also a strong stable isotope signal in the organic matter discharged by the mill. Chlorolignin, isolated from the effluent, had a δN^{15} of −4.4 ‰ and a δC^{13} value of −27.1‰, compared with average values of +2.2‰ and −27.8‰ for the trapped material at station 2 (Tables 6 and 7). Thus, the isotopic composition of nitrogen is a better tracer of mill derived organic matter than carbon.
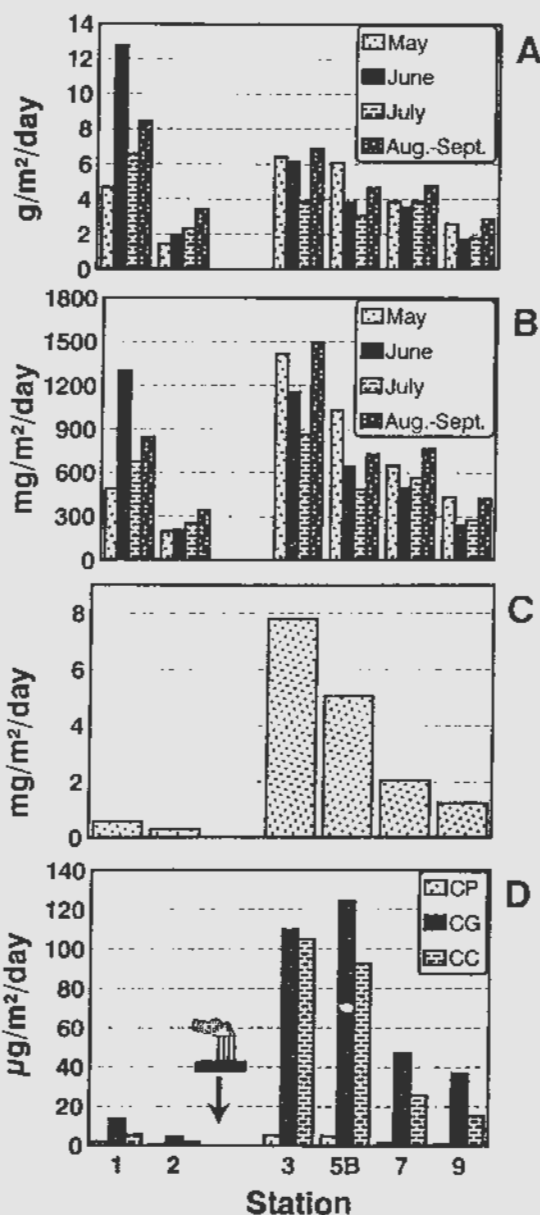

Fig. 4. The calculated maximum sedimentation of suspended particles (A) and organic carbon (B) at different stations during the summer 1991 and the maximum sedimentation of SOX (C) and chlorophenolics (D) at different station during the 'May' sampling period. The exact dates for sampling are shown in Table 4.

Table 4
Organic carbon content (% of dry wt. ± S.D., $n = 3$) of the sediment trap material and the sediment at the stations

Station (km)	May 10.5.–11.6.	June 11.6.–12.7.	July 12.7.–15.8.	Aug.–Sept. 15.8.–8.10.	Sediment ($n = 5$)
–8.5	10.46 ± 0.31	10.20 ± 0.02	10.26 ± 0.49	10.03 ± 0.01	6.86 ± 0.53
–6	13.67 ± 0.51	11.12 ± 0.01	10.93 ± 0.02	10.05 ± 0.10	na
3	22.09 ± 0.43	18.89 ± 0.24	22.33 ± 0.47	21.78 ± 0.02	19.70 ± 1.63
9	16.97 ± 0.39	16.76 ± 0.94	15.92 ± 0.24	15.64 ± 0.01	14.00 ± 1.90
12	16.86 ± 0.26	14.04 ± 0.03	14.70 ± 0.18	16.04 ± 0.19	11.53 ± 1.39
16	16.62 ± 0.36	14.18 ± 0.56	15.24 ± 0.16	14.50 ± 0.27	12.51 ± 0.48

na = not analyzed.

Table 5
Nitrogen content of the sediment trap material (% ± S.D., $n = 3$) and the sediment at the stations

Station (km)	May 10.5.–11.6.	June 11.6.–12.7.	July 12.7.–15.8.	Aug.–Sept. 15.8.–8.10.	Sediment ($n = 5$)
–8.5	0.87 ± 0.05	0.89 ± 0.01	0.95 ± 0.12	1.07 ± 0.01	0.57 ± 0.03
–6	1.08 ± 0.03	0.95 ± 0.01	1.40 ± 0.09	1.27 ± 0.02	na
3	1.70 ± 0.08	1.50 ± 0.09	1.91 ± 0.04	1.46 ± 0.04	1.26 ± 0.18
9	1.57 ± 0.10	1.88 ± 0.08	1.71 ± 0.01	1.36 ± 0.02	0.97 ± 0.12
12	1.73 ± 0.01	1.44 ± 0.03	2.04 ± 0.02	1.85 ± 0.12	0.89 ± 0.14
16	1.58 ± 0.04	1.40 ± 0.10	1.78 ± 0.04	1.94 ± 0.19	0.99 ± 0.06

na = not analyzed.

Table 6
δC^{13} of organic carbon (‰) from the sediment trap material and the sediment at the stations

Station (km)	May 10.5.–11.6.	June 11.6.–12.7.	July 12.7.–15.8.	Aug.–Sept. 15.8.–8.10.	Sediment
–8.5	–27.6	–25.9	–29.1	–27.0	–27.2
–6	–30.1	–27.4	–26.6	–27.2	–27.4
3	–28.4	–28.9	–28.8	–27.12	–28.3
9	–30.1	–28.6	–26.9	–30.7	–28.3
12	–32.0	–28.5	–28.5	na	–28.3
16	–31.9	–29.1	–26.8	–28.3	–28.3

na = not analyzed. Pulp mill chlorolignin had a value of –27.1.

Table 7
δN^{15} of nitrogen (‰) from the sediment trap material and the sediment at the stations

Station (km)	May 10.5.–11.6.	June 11.6.–12.7.	July 12.7.–15.8.	Aug.–Sept. 15.8.–8.10.	Sediment
–8.5	2.1	2.1	3.4	2.4	1.8
–6	0.6	1.8	3.3	3.2	1.7
3	–3.6	–1.4	–1.0	–2.3	–2.3
9	–1.1	–0.5	2.3	0.7	–0.5
12	–0.2	1.3	3.4	1.1	1.1
16	–0.7	1.8	na	3.3	1.8

na = not analyzed. Pulp mill chlorolignin had a value of –4.4.

Concentrations of chlorophenolics were 2–8 times higher in the trapped particles collected downstream from the mill than in the ones upstream (Fig. 5; Appendix 1). The concentrations

decreased further downstream but did not reach upstream levels within the recipient area studied. The concentration of pentachlorophenol (PCP) did not show much change. SOX (total organically
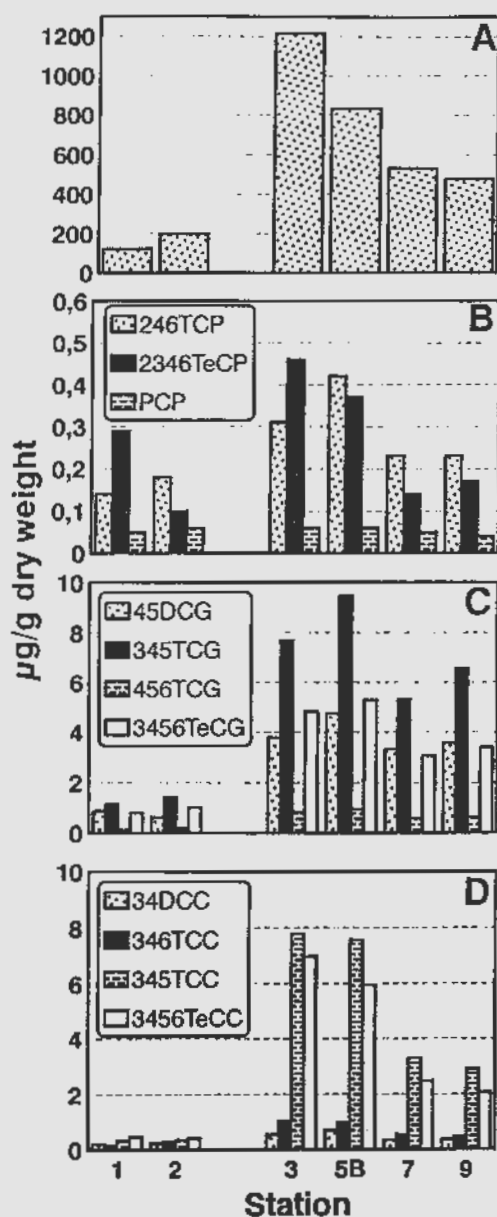

Fig. 5. SOX (A) chlorophenol (B) chloroguaiacol (C) and chlorocatechol (D) concentrations in sedimented particles on the 'May' 1991 sampling period. For the codes, please, see Table 2.
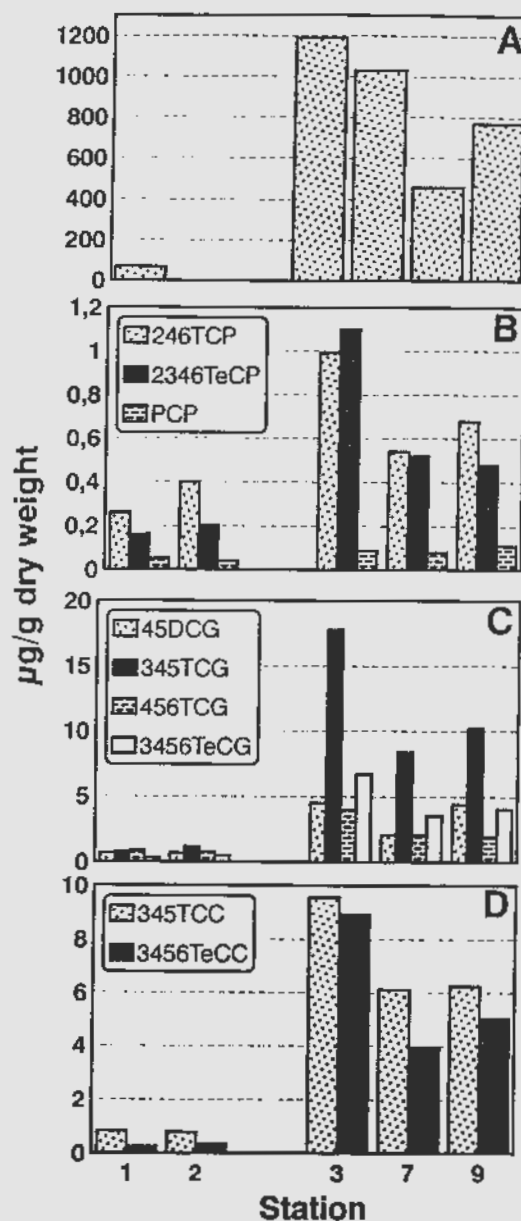
Fig. 6. SOX (A) chlorophenol (B) chloroguaiacol (C) and chlorocatechol (D) concentrations in the sediment from the same stations where sediment traps were placed. For the codes, please, see Table 2. (The SOX data is from the reference 39).

bound halogens) in particles showed a similar trend as the identified chlorinated compounds, although these identified compounds form only 1–2% of measured SOX in the particles.

3.2. Sediments

Sediments downstream of the mill showed elevated concentrations of organic carbon (Table 4), SOX and chlorophenols (Fig. 6; Appendix 1) and the isotopic signatures (Tables 6 and 7) altered by the effluent. Organic carbon concentration in the sediments at station 3 were approximately 3 times that of the background at station 2, and concentrations were still double the background value at station 9. Also, the concentrations of chlorophenolics were higher in the sediment (Fig. 6) than in the sedimenting particles (Fig. 5) at each station possibly showing the effect of changing the bleaching process at the mill from the use of molecular chlorine to elemental chlorine free (ECF) bleaching.

The elevated sediment organic matter clearly shows the influence of mill effluent nitrogen (δN^{15} 6.7‰ lighter than the average of trap material at station 2) in its' isotopic composition (Table 7); sediment values are approximately 0.5‰ lighter than the mass weighted trap average at each station. Although our 1 sample of mill effluent chlorolignin had a δC^{13} value similar to background trap materials, at stations 1–3 the sediment δC^{13} (Table 5) is the same as the mass weighted trap value for the entire collection period, while the trap stations further downstream from the mill effluent average approximately 1‰ lighter than the sediments. The source of this light material is most likely from primary production in the lake.

4. Discussion

Calculated sedimentation rates of SOX and chlorophenolics from the traps show that chloroguaiacols and chlorocatechols have a high sedimentation near the pulp mill, but chlorophenols are not as strongly affected (Fig. 4). Sediment traps are excellent devices for sampling the pool of materials settling out of the water column. They

have been used extensively and their collection bias and efficiency thoroughly investigated [33–35]. There is extensive evidence that traps deployed close to lake bottom collect both sedimenting and resuspended particles [9,11,13,14]. Questions have also been raised about microbial decomposition of trapped organic matter [36] or actively swimming zooplankton entering the traps [37]. However, with all these potential sources of interference, traps are still the best devices for measuring the downward flux of particulate matter [38].

In this study, traps have been employed to examine the role of particulate material on the transport of chlorophenolics eminating from a point source. We know from the spatial patterns of chlorophenolics in sediments that a fraction of the effluent is being deposited. When we use the δN^{15} of the organic matter of the mill effluent and the upstream (stations 1 and 2 average) organic matter as stable end members, we can estimate the fraction of effluent in the downstream traps. We can apply a similar approach to the sediments.

$$\delta N^{15} \ DS = x * \delta N^{15} \ (\text{mill effluent}) + (1 - x) * \delta N^{15} \ (\text{Background})$$

where

DS is the downstream trap or sediment sample, and x is the fraction of effluent.

These estimates, presented in Table 8, show consistent results except for the first trapping period. The organic matter in station 3 is composed of

Table 8
Fraction of effluent materials in traps and sediments downstream of the mill based on δN^{15}

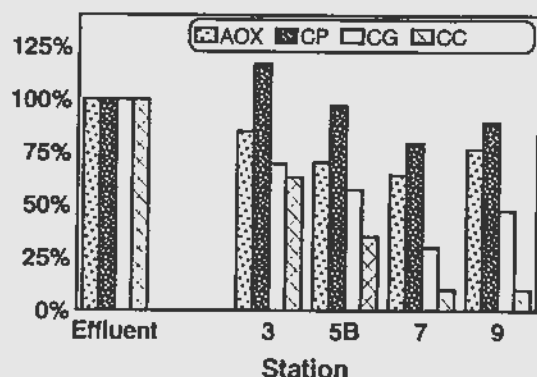| Station (km)	May 10.5.– 11.6.	June 11.6.– 12.7.	July 12.7.– 15.8.	Aug.– Sept. 15.8.– 8.10.	Sediment
3	0.86	0.53	0.56	0.71	0.66
9	0.43	0.39	0.14	0.29	0.37
12	0.27	0.10	−0.01	0.24	0.11
16	0.36	0.02	na	−0.07	−0.01

na = not analyzed.

Fig. 7. The relative concentrations of AOX and chlorophenolics in the pulp mill effluent (= 100%) and along the recipient. CP = the sum of measured chlorophenols, CG = the sum of measured chloroguaiacols, and CC = the sum of measured chlorocatechols

53–71% mill effluent and this contribution declines through the subsequent traps and sediment samples to a background value at station 9. The mill contribution is greater during the first collection period and approximately 30% of the trapped organic matter at station 9 is mill effluent. One explanation for this could be that during the long winter period with ice cover on the area some of the effluent discharged is stored near the bottom on this area and then during the spring turn over period, which happens to be in May in southern Lake Saimaa, this material is reintroduced to the lake system. The δN^{15} tracer disappears faster than the organic carbon and nitrogen concentrations (Table 4 and 5), which are still about 50% above background at station 9. This discrepancy is either due to isotopic fractionation as the material moves downstream or a third source of organic nitrogen between the effluent and station 9. With the samples available, we cannot separate these two alternatives.

A complementary calculation can be made for the dissolved constituents, using sodium as a conservative tracer.

$$\text{dilution} = \frac{Na^+(px) - Na^+(up)}{Na^+(ef)}$$

where $Na^+(px)$ is the sodium concentration at different stations along the recipient, $Na^+(up)$ is the sodium concentration upstream from the mill and $Na^+(ef)$ is the sodium concentration in the pulp mill effluent. The relative freely dissolved concentrations (corrected for dilution) of chlorophenolics (Fig. 7) showed that the chlorophenols mostly remain in the water and flow through the system. On the other hand, only about 40% of chloroguaiacols and 10% of chlorocatechols are found at the furthest station. Part of this loss can be accounted for by sedimentation, but as yet biological and chemical degradation rates of these compounds are not known in this system and are likely contributing to the loss. Similar to chlorophenols, most of the AOX pass through the system (Fig. 7) and do not sediment within the recipient area.

The SOX and chlorophenolic concentrations in the sediment samples from the area were somewhat higher that in sedimenting particles (Figs. 5 and 6), but the sediment samples were taken at different time of the year than the sedimenting particles were collected, so the comparison cannot be that exact. On the other hand, high sediment concentrations may express the high chlorine use of bleaching during the previous years before the changes in the bleaching process.

Appendix 1.

Chlorophenolic concentration data for May, 1991 water, trap, and surface sediment samples

Water samples		Dissolved free (µg/l)								
Station	km	P1	P2	PCP	C1	C2	G1	G2[a]	G3	G4
2	−6	0.011	0.014	0.007	0.005	0.010	0.027	0.026	0.022	0.008
Mill	0	7.1	1.1	0.3	4.30	46.80	7.40	8.60	19.00	6.40
3	3	0.282	0.069	0.049	0.440	0.197	0.159	1.35	0.177	0.230
5	9	0.123	0.119	0.019	0.039	0.058	0.104	0.308	0.017	0.056
7	12	0.115	0.053	0.021	0.041	0.037	0.097	1.627	0.046	0.053
9	16	0.070	0.044	0.027	0.020	0.025	0.105	1.747	0.036	0.038

[a] some problems to identify the compound, may be two peaks together (data not shown in Fig. 3)

Sediment trap		Trap total (µg/g dry matter)									Mass	
Station	km	P1	P2	PCP	C1	C2	G1	G2	G3	G4	SOX	Flux (g/m²/d)
1	−8.5	0.14	0.29	0.05	0.34	0.46	0.88	1.16	0.13	0.8	100	4.67
2	−6	0.18	0.1	0.06	0.36	0.42	0.62	1.44	0.19	1.02	200	1.43
Mill	0											
3	3	0.31	0.46	0.06	7.78	6.97	3.78	7.69	0.84	4.84	1200	6.41
5	9	0.42	0.37	0.06	7.56	5.95	4.75	9.45	0.94	5.29	800	6.09
7	12	0.23	0.14	0.05	3.29	2.48	3.32	5.32	0.58	3.05	525	3.85
9	16	0.23	0.17	0.04	2.9	2.07	3.57	6.56	0.63	3.39	450	2.6

Sediment		Sediment total (µg/g dry)									
Station	km	P1	P2	PCP	C1	C2	G1	G2	G3	G4	SOX
1	−8.5	0.26	0.16	0.050	0.84	0.24	0.67	0.77	0.84	0.31	50
2	−6	0.4	0.2	0.040	0.78	0.34	0.65	1.15	0.76	0.47	na
Mill	0										
3	3	0.99	1.1	0.090	9.55	8.92	4.52	17.79	3.97	6.69	1200
5	9	0.86	1.11	0.060	10.15	8.96	3.27	14.15	4.06	5.52	1025
7	12	0.54	0.52	0.080	6.11	3.94	2.06	8.38	2.06	3.53	450
9	16	0.68	0.48	0.110	6.24	5.03	4.38	10.23	1.91	4.04	750

P1 = 246TCP   P2 = 2346TeCP
C1 = 345TCC   C2 = 3456TeCC
G1 = 45DCG   G2 = 345TCG   G3 = 456TCG   G4 = 3456TeCG

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